

# PROBLEMS OF QUALITY

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## PROBLEMS OF ESTIMATING GLASS BATCH QUALITY

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Problems arising in estimating the quality of glass batches are discussed and methods for solving them are proposed.

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All companies producing equipment for batch-preparation divisions confront the problem of estimating the quality of their performance. If only proportioning equipment is installed, it is possible to restrict oneself to the accuracy of proportioning.

The Stromizmeritel' JSC implements an integrated approach to batch-preparation divisions: it designs, develops, produces, and installs equipment for the entire technological cycle, from receiving and treating raw materials to charging batch and cullet into the hoppers of the glass-melting furnace loaders. Consequently, the performance has to be estimated based on the batch quality.

In 1977 the Ministry of Construction Materials of the USSR approved the Regulations on Operation of Container Glass Factories (hereafter called "The Regulations"), which specify in detail the sampling methods, as well as the types and methods of chemical analyses of glass batch and methods for estimating batch quality. Prior to 2003, factories developed their company standards in accordance with these Regulations, extending and refining the content of the Regulations as applied to the local conditions.

At the end of 2003 the Khrustal' Central Chemical Institute approved standards on sampling methods and method of analysis of soda-sulfate batch [1, 2]. These standards were supposed to summarize the experience accumulated in 26 years of using the Regulations and offer it to industrial companies.

The standard on the methods of analysis [2] merits a detailed consideration. In addition to the methods included in the Regulations, it includes the analytical methods of hydrochloric acid titration and Trilon B titration at the stage of preparation for the corresponding analysis; moreover, corrective coefficients are introduced in the formulas for calculating the results of analysis. This prevents the distortion of analytical results related to the parameters of the corresponding solutions.

The important merits of standard [2] include the analysis of carbonate content using Trilon B titration and the determination of sulfate content by the chemicals method. This makes it possible to eliminate the defects of the calculation formulas contained in the Regulations for determining weight contents of carbonates and sulfate.

However, unlike the Regulations, standard [2] in the denominator of the formulas indicates the value  $m$  defined as "the batch sample in g." The Regulations give a more exact definition in the corresponding formulas, whenever they are indicated: "initial dry batch sampling in g," which prevents misunderstanding.

The item of the standard called "The determination of batch homogeneity" leads to questions, since it reads: "A conclusion on batch homogeneity is made on the basis of the comparison between the results of analysis and the prescribed batch formula." The batch formula has no direct data on the specified values. To estimate the homogeneity of a batch, it is sufficient to compare the results of three independent samples. At the same time, standard [2] lacks a section on the classification of batches by categories.

Considering that factories use the methods described in the Regulations, the subsequent discussion is based on these Regulations.

According to Appendix 4 of the Regulations, the batch quality check and the determination of its category is conducted by a laboratory based on the following analyses: determination of batch moisture and the content of soda, water-insoluble precipitate, and acid-insoluble precipitate.

Based on the results of these analyses, the following reference values expressed in percent are determined:

batch moisture;

quantity of water-insoluble residue  $IR_{H_2O}$ ;

quantity of soda in the batch  $Q_{Na_2CO_3}$ ;

quantity of residue insoluble in acid  $IR_{HCl}$

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and the following values are calculated:

total content of calcium and magnesium carbonates from the formula

$$L_c = IR_{H_2O} - IR_{HCl};$$

content of sodium sulfate from the formula

$$L_s = 100 - (IR_{H_2O} - Q_{Na_2CO_3}).$$

To determine the batch categories the Regulations propose an approach in which “the degree of incompliance of the batch composition with the preset batch formula is identified as the category of the batch. The maximum deviation from the batch composition ( $\pm$  even in one of the components) from the preset formula corresponds to the following categories: I) 0 – 0.20, II) 0.21 – 0.40, III) 0.41 – 0.60, IV) 0.61 – 0.80, V) 0.81 – 1.00”.

The Regulations and publications [1 – 3] describe in detail the chemical process of performing analyses, but the literature lacks a description of methods for calculating reference values for comparing and computing deviations, or detailed mathematical analysis based on the theory of errors. An analysis of the quality of the batch in implementing and operating dosing-and-mixing lines shows that errors in formula calculation or in estimating the results of the chemical analysis of the batch are frequently regarded as failures of the proportioning equipment. In this context, the management of the Stromizmeritel’ JSC in 1997 set the task of developing a universal program for the calculation of batch formulas [4] including the option of obtaining reference values to estimate the batch quality (a theoretical composition). However, the comparison of the formulas used at six different companies in 1997 – 1998 indicated that, despite the outward similarity of the formulas, there is no unified approach to this problem. The literature does not yet offer an analysis of this subject.

All formulas had a common expression for calculating reference values based on analyses, which is a sum of the contributions of the individual batch components to the result of analysis. The contributions of single components to the sum do not affect each other and depend only on the component and the type of analysis.

The program contained a flexible mechanism for specifying formulas, which allowed for application of virtually any formulas accepted at particular factories. To set a formula, the contribution of each component to the result of each analysis is specified. Below is an example of such specification for dolomite:

Analysis	Oxide	Coefficient
$IR_{H_2O}$	All	1.00
$IR_{HCl}$	$SiO_2$	1.00
$IR_{HCl}$	$Al_2O_3$	1.00
$IR_{HCl}$	$Fe_2O_3$	1.00
Carbonates	CaO	1.78
Carbonates	MgO	2.09

During the implementation of this program for calculating batch formulas, formulas for the reference values in different types of analysis were refined and the reasons for differences in the formulas of most factories were identified.

The least clear is the calculation of the batch moisture. The reference value of moisture is initially set to determine the quantity of water to be added in batch mixing. The calculation program provides for the possibility of taking into account the moisture of all materials. The calculations of the quantity of water added were verified at numerous factories and found correct. However, experimental verification shows that feeding a calculated amount of water yields a moisture level that is several fractions of a percent lower than it should be. This value is not always stable; one of the possible reasons may be the reaction of water with batch components. Therefore, all factories experimentally determine the quantity of water to be added in mixing based on the resulting batch moisture and periodically adjust this quantity.

The determination of the content of soda in a batch was always regarded as the simplest analysis in estimating batch quality. According to the Regulations, the content of soda in a batch is calculated in filtrate and in rinsing water in titration in 2 N HCl with methyl orange indicator based on the following formula:

$$Q_{Na_2CO_3} = \frac{100KT}{C_1},$$

where  $Q_{Na_2CO_3}$  is the soda content in the batch, %;  $K$  is the amount of HCl solution used for titration, ml;  $T$  is the HCl solution titer for soda, g/ml; and  $C_1$  is the initial dry batch sample, g.

However, although titration is known to determine the content of  $Na_2CO_3$ , many producers calculate the reference value for this analysis based on the following formula:

$$P_s = \frac{W_s}{W_{100}},$$

where  $W_s$  and  $W_{100}$  is the total quantity of soda and the total quantity of batch required for melting 100 kg of glass, kg.

This formula is true only in the case where the batch calculation is performed for soda with 100% basicity of  $Na_2CO_3$ . In other cases, deviations from the reference value may reach a few fractions of a percent. Furthermore, it should be taken into account that  $Na_2CO_3$  is introduced into the batch by other components as well, for instance, by feldspar. The accepted analysis does not always allow us to identify  $Na_2CO_3$  introduced via feldspar, although it should be taken into account in calculating batch formulas.

For an appropriate calculation of the reference value for this analysis, the program uses the following formula:

$$Q_{Na_2CO_3} = \frac{S_{Na_2CO_3}}{W_{100}},$$

where  $Q_{Na_2CO_3}$  is the reference value of the content of

$\text{Na}_2\text{CO}_3$  in the batch found by analysis and  $S_{\text{Na}_2\text{CO}_3}$  is the quantity of  $\text{Na}_2\text{CO}_3$  introduced into the batch via soda (to melt 100 kg of glass).

The value  $S_{\text{Na}_2\text{CO}_3}$  is always present in the final formula calculation table, which specifies the quantity of  $\text{Na}_2\text{CO}_3$  introduced via soda. If the initial data specify the content of  $\text{Na}_2\text{O}$  for soda, the following additional coefficient should be introduced:

$$S_{\text{Na}_2\text{CO}_3} = 1.71 S_{\text{Na}_2\text{O}},$$

where  $S_{\text{Na}_2\text{O}}$  is the quantity of  $\text{Na}_2\text{O}$  introduced into the batch via soda (to melt 100 kg of glass) and 1.71 is the conversion coefficient obtained from the ratio of the atomic weight of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{O}$ .

The program for batch formula calculation includes the following line for soda:

Analysis	Oxide	Coefficient
Alkali (soda)	$\text{Na}_2\text{O}$	1.71

The content of other components does not affect this analysis.

The method for determining the content of water-insoluble residue is described in the Regulations and in the standard [1]. The reference value for the content of water-insoluble residue is usually calculated based on one of the two formulas:

$$P_{\text{IR}_{\text{H}_2\text{O}}} = \frac{W_{100} - W_s - W_{\text{sul}} - W_{\text{salt}}}{W_{100}},$$

where  $W_s$ ,  $W_{\text{sul}}$ , and  $W_{\text{salt}}$  are the quantities of soda, sulfate, and saltpeter required for melting 100 kg of glass  $W_{100}$  (if a material is not included in the formula, the corresponding quantity is equal to zero), kg;

$$P_{\text{IR}_{\text{H}_2\text{O}}} = \frac{W_{\text{sand}} + W_d + W_{\text{fs}} + W_{\text{ch}}}{W_{100}},$$

where  $W_{\text{sand}}$ ,  $W_d$ ,  $W_{\text{fs}}$ ,  $W_{\text{ch}}$  are the quantities of sand, dolomite, feldspar or aluminum, chalk or lime, and other components insoluble in water required to melt 100 kg of glass.

The above formulas are equivalent and pose no questions. For using them, the batch calculation program should contain the following line for taking into account all components insoluble in water in the analysis:

Analysis	Oxide	Coefficient
$\text{IR}_{\text{H}_2\text{O}}$	All	1.00

The biggest problem for a correct estimate is the analysis of carbonate content in the batch. The Regulations, as well as

publications [1–6], offer two approaches to solving this problem: determination of the content of residue insoluble in HCl and Trilon B titration of the solution in HCl.

*The first method* is so far the more widely used (it is the only method indicated in the Regulations) and requires less time. However, one should understand the problems related to this method.

In determining a reference value to compare it with the results of analysis of a water-insoluble residue one should bear in mind that the solubility of feldspar in acid may vary from 18 to 28% and cannot be calculated based on oxide content. If one neglects this fact, the error in the reference value may reach 2%. To solve this problem, when a new supply of feldspar is received, its solubility in HCl is analyzed and the obtained result is used as the coefficient in the formula for calculating the reference value. Such method has been long used at the Salavatsteklo Company.

According to the data from the laboratory at the Aktis Company (city of Novocherkassk), it is not only feldspar that has variable solubility in acid; in other materials solubility varies within narrow limits. For instance, the solubility of sand in HCl may reach 2%, which contributes perceptible distortions to the reference value.

When calculating the reference value of water-insoluble residue for dolomite, lime, and chalk, many producers take into account only  $\text{SiO}_2$  content, neglecting the presence of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in these components, although the latter do not dissolve in HCl either.

The resulting content of acid-insoluble residue obtained in analysis at the factories using this method is accepted as the reference analysis and named “the sand percent.” We have encountered no less than five formulas for calculating the reference value in performing this analysis. There is no sense to consider those in the present paper, since the only formula that can be recognized as suitable for analysis in any conditions is the following one:

$$P_{\text{IR}_{\text{HCl}}} = \frac{W_{\text{sand}} + W_{\text{fs}} K + S_{\text{SiO}_2} + S_{\text{Al}_2\text{O}_3} + S_{\text{Fe}_2\text{O}_3}}{W_{100}},$$

where  $K$  is the feldspar insolubility coefficient defined as 100% solubility of feldspar in acid multiplied by 0.01; and  $S_{\text{SiO}_2}$ ,  $S_{\text{Al}_2\text{O}_3}$ , and  $S_{\text{Fe}_2\text{O}_3}$  are the total quantities of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  introduced into the batch (for melting 100 kg of glass) by all components except for sand and feldspar (these value can be easily calculated from the final table of the formula calculation).

Assuming that the insignificant quantities of CaO and MgO contained in sand dissolve in HCl, the formula takes the following form:

$$P_{\text{IR}_{\text{HCl}}} = \frac{\sum \text{SiO}_2 + \sum \text{Al}_2\text{O}_3 + \sum \text{Fe}_2\text{O}_3 - W_{\text{fs}}(1 - K)}{W_{100}},$$

where  $\sum \text{SiO}_2$ ,  $\sum \text{Al}_2\text{O}_3$ , and  $\sum \text{Fe}_2\text{O}_3$  are the total quantities of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  introduced into the batch (for

melting 100 kg of glass) by all components (these values are shown in the bottom line of the final table of the batch formula calculation).

The program for the batch formula calculation should include the following lines for each material containing the specified oxides:

Analysis	Oxide	Coefficient
IR <sub>HCl</sub>	SiO <sub>2</sub>	1.00
IR <sub>HCl</sub>	Al <sub>2</sub> O <sub>3</sub>	1.00
IR <sub>HCl</sub>	Fe <sub>2</sub> O <sub>3</sub>	1.00

For sand this line should have the following form:

Analysis	Oxide	Coefficient
IR <sub>HCl</sub>	All	1.00

For feldspar if, for instance, its solubility in acid is equal to 26%, the line should have the following form:

Analysis	Oxide	Coefficient
IR <sub>HCl</sub>	All	0.74

The second method is described in detail in the standard [2]. Although it is more labor-consuming, it provides higher stability and accuracy. Using this method, one should bear in mind that titration is performed in two stages and, depending on the formulas for processing the results of analysis, different coefficient values are possible in the formula for calculating the reference value, which is computed from the formula:

$$P_c = \frac{K_1 S_{\text{CaO}} + K_2 S_{\text{MgO}}}{W_{100}},$$

where  $S_{\text{CaO}}$  and  $S_{\text{MgO}}$  are the total quantities of CaO and MgO introduced into the batch (for 100 kg of glass) by all materials (these values are given in the bottom line of the final table for formula calculation);  $K_1 = 1.78$  is the coefficient for converting CaO into CaCO<sub>3</sub> found through the ratio of their atomic weights; and  $K_2$  can take a value of 2.09 (conversion coefficient of MgO to MgCO<sub>3</sub>) or 2.49 (conversion coefficient of MgO to CaCO<sub>3</sub>) depending on processing analysis data.

The programs for calculating formulas should have the following lines for each material containing these oxides:

Analysis	Oxide	Coefficient
Carbonates	CaO	1.78
Carbonates	MgO	2.09 or 2.49

As was mentioned earlier, the Regulations propose the following formula for determining sodium sulfate content:

$$L_s = 100 - (\text{IR}_{\text{H}_2\text{O}} - Q_{\text{Na}_2\text{CO}_3}).$$

The accuracy of the results of chemical analysis is 0.3% [5, 6]. Thus, by the theory of errors, the accuracy of the content of sulfate will be equal to 0.6%. Since its content often is at the level of 0.3 – 0.5%, it may occur that the content of sulfate estimated based on the results of analysis is less than zero. This cannot be attributed to a proportioning error or to other violations of the batch-preparing technology. Such situations have been registered in the operation of the proportioning-mixing line at the Rostovsteklo Works (Rostov-on-Don) in 2003 – 2004.

Thus, it can be concluded that the parameter  $L_s$  is inadmissible as a reference value in determining the category of the batch. Standard [2] offers an alternative to this formula. However, the analysis of the content of Na<sub>2</sub>SO<sub>4</sub> proposed in this standard is labor-consuming and its application at factories has not been registered.

A similar conclusion can be made for determining the total content of calcium and magnesium carbonates, which, according to the Regulations, is found from the difference between water-insoluble and acid-insoluble residue. This analysis should be performed using the Trilon B titration method proposed in standard [2], which is already used by many companies.

To avoid the specified problems, the parameters used to determine a batch category should be only direct analytical results (batch moisture, quantity of water-insoluble residue, soda content in the batch; quantity of acid-insoluble residue, content of carbonates found by the titration method, and carbonate content found by the precipitation method). Even in this case the error in determining the batch category may be equal to 1.5 category (0.3%). In the case of using calculated parameters (total carbonate content found from the specified difference and sulfate content), the error may reach 3 categories (0.6%) and does not reflect the real batch quality.

The Regulations indicate that the batch category is determined based on the maximum deviation from the batch composition ( $\pm$  at least in one of the components), but considering substantial errors in determining categories committed in the industrial experience, we proposed using a category index averaged over all analyses, except for the cases where at least one analysis yields a quality parameter worse than category V (a deviation over 1%). The transition to three categories proposed in standard [2] is likely to be supported by the companies. However, it is desirable to develop precise and justified methods for calculating the batch category and estimating batch homogeneity.

The six-years experience of using the program of calculating batch formulas based on reference values corroborates the validity of the approach described in this paper. This program has been implemented at 20 glass factories; it provided universality in calculating reference values and is not re-

stricted to the above types of analyses, which makes it possible to add formulas for other analyses (for instance, the analysis using boric acid implemented at the URSA Chudovo Company).

## REFERENCES

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